DESCRIPTION

EXHAUST-GAS PURIFYING CATALYST

TECHNICAL FIELD

The present invention relates to an exhaust-gas purifying catalyst, and particularly to an exhaust-gas purifying catalyst as a catalyzer for purifying hydrocarbons, carbon monoxide, nitrogen oxides and the like contained in exhaust gas exhausted from an internal combustion engine.

BACKGROUND ART

Regulations of exhaust gas of vehicles are being spread worldwide. Also in Japan, because regulations of exhaust gas of gasoline-powered vehicles have been strengthened since 2,000, there have been developed and used catalysts each comprising a substrate such as a honeycomb made of cordierite coated with a carrier such as Al_2O_3 (alumina) which is a porous oxide carrying noble metal particles such as Pt (platinum), Pd (palladium) or Rh (rhodium), aiming at a fuel reforming catalyst and an exhaust-gas purifying catalyst for vehicles.

Then arises a problem that the catalyst amount to be used per one vehicle is increased correspondingly to the strengthened regulations of exhaust gas so that the noble metal amount to be used per one vehicle is also increased, thereby increasing costs of vehicles. This leads to a problem of resource exhaustion in a fuel cell technique getting a lot of attention to solve recent energy resource problems, and global warming problems accompanying to carbon dioxide emission, because noble metal is used as catalysts even in the fuel cell technique. Thus, it is necessary to decrease the noble metal amount to be used in the catalysts.

Catalytic activities of noble metals are substantially proportional to surface areas of the noble metals, respectively, because reactions utilizing the noble metals are contact-catalytic reactions to be progressed

at the noble metal surfaces, respectively. Therefore, to obtain the maximum catalytic activity from a small amount of noble metal, it is necessary to prepare noble metal particles having smaller particle diameters and larger specific surface areas.

However, in case of fine particles of noble metal having particle diameters of 1nm or less, the noble metal particles are extremely unstable because they have higher surface reactivities and larger surface energies. Thus, the noble metal particles are apt to approach each other and tend to cause sintering. Particularly, Pt considerably sinters when heated. Thus, even when noble metal particles are dispersedly carried on a carrier, particle diameters are increased due to sintering by heating, thereby deteriorating a catalytic activity. It is thus difficult to maintain the catalytic activity in the fine particle state, since catalysts for vehicles are exposed to high temperatures usually from 800 to 900°C, and to high temperatures exceeding 1,000°C in some cases. As such, sintering of noble metal is the most difficult point, in establishing an exhaust-gas purifying catalyst with a small amount of noble metal.

Meanwhile, it has been also demanded to develop inexpensive catalyst materials other than noble metals, so as to limit usage of noble metals. For example, costs might be remarkably decreased, if transition metals and the like are usable as catalyst materials. Even up to now, catalysts utilizing noble metals and other metals have been proposed. Disclosed in JP-A-59-230639 is a catalyst including a honeycomb substrate which carries activated alumina carrying: at least one kind selected from cerium (Ce), zirconium (Zr), iron (Fe) and nickel (Ni); at least one kind selected from neodymium (Nd), lanthanum (La) and praseodymium (Pr) if required; as well as at least one kind selected from Pt, Pd and Rh (see patent-related reference 1). Further, proposed in Japanese Patent No. 3251009 is another exhaust-gas purifying catalyst comprising one or more kinds of oxides of any one of Co (cobalt), Ni

(nickel), Fe (iron), Cr (chromium), and Mn (manganese), and at least one kind of Pt, Rh, and Pd, in which that one kind of oxide and that one kind of Pt, Rh, and Pd dissolve in each other into a state of solid solution at interfaces where they contact with each other, so that the catalyst is configured to exhibit an ability for purifying exhaust gas of internal combustion engines and the like at temperatures of 250°C or lower.

DISCLOSURE OF INVENTION

However, transition metals have no catalytic activities in themselves, and it has been impossible to improve catalytic activities to decrease usage amounts of noble metals insofar as based on any of the conventional methods.

The present inventors have earnestly and repeatingly studied to solve the above-mentioned conventional techniques and the problems, and resultingly found such a unique phenomenon that exhaust-gas purifying performances are improved by a configuration in which a noble metal and a transition metal compound having a metallic portion are carried on the same porous carrier such that the noble metal and the transition metal compound are contacted with each other, thereby narrowly completing the present invention.

Namely, the present invention solves the above-mentioned problem, by providing an exhaust-gas purifying catalyst comprising: at least one kind of noble metal selected from Ru, Rh, Pd, Ag, Ir, Pt, and Au; a transition metal compound including at least one kind of transition metal element selected from Mn, Fe, Co, Ni, Cu, and Zn, the transition metal compound having a metallic portion; and a porous carrier carrying the noble metal and the transition metal compound.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is an explanatory view of an exhaust-gas purifying catalyst

according to an embodiment of the present invention;

FIG. 2 is an explanatory view of another configuration of the exhaust-gas purifying catalyst according to the embodiment of the present invention;

FIG. 3 is a graph of data measured by XPS, and peaks obtained therefrom by peak separation;

FIG. 4 is a graph of purifying ratios of Examples and Comparative Examples after endurance; and

FIG. 5 is an explanatory graph of a relationship between usage amount of platinum and purifying ratio.

BEST MODE FOR CARRYING OUT THE INVENTION

Embodiments of the exhaust-gas purifying catalysts according to the present invention will be described hereinafter. In the exhaust-gas purifying catalysts of these embodiments, each exhaust-gas purifying catalyst comprises: at least one kind of noble metal selected from Ru (ruthenium), Rh (rhodium), Pd (palladium), Ag (silver), Ir(Iridium), Pt (platinum), and Au (gold); a transition metal compound including at least one kind of transition metal element selected from Mn (manganese), Fe (Iron), Co (cobalt), Ni (nickel), Cu (copper), and Zn (zinc), and the transition metal compound having a metallic portion; and a porous carrier carrying the noble metal and the transition metal compound.

Shown below are exhaust-gas purifying reactions, i.e., those reactions for purifying hydrocarbons (HC's), carbon monoxide (CO) and nitrogen oxides (NOx) which are harmful components in exhaust gas.

(Chemical formula 1)

$CO+(1/2)O_2 \rightarrow CO_2$···formula (1)

$NOx+H_2 \rightarrow N_2+H_2O$···formula (2)

$NOx+CO \rightarrow CO_2+N_2$···formula (3), and

$HC+O_2 \rightarrow H_2O+CO_2$···formula (4).

The respective harmful components are adsorbed onto the noble metal inherently having a higher activity by itself, and thus the reactions are progressed. The catalytic activity is kept even when the noble metal is decreased in amount, by virtue of the coexistence of the noble metal and the transition metal compound which hardly exhibits a catalytic activity by itself, on the same porous carrier.

The reason of the above is considered to be based on occurrence of a phenomenon called "spillover" where hydrogen in exhaust gas is initially and dissociatively adsorbed onto a surface of the noble metal and then migrates to a surface of the transition metal compound to thereby reduce NOx on the surface of the transition metal compound under a so-called stoichiometric condition where an oxygen amount and a reductant amount in exhaust gas are identical in ratios. Namely, it is considered that the noble metal and the transition metal compound contact with each other to thereby form a composite so that the noble metal acts as an adsorbing site for adsorbing hydrogen, and thus the transition metal compound is activated to function as a catalytic site. In this way, establishment of the state where hydrogen is apt to reach the transition metal compound, facilitates obtainment of a state where an exhaust-gas purifying activity is easily achieved, i.e., obtainment of a reducing state, thereby improving the exhaust-gas purifying catalytic activity.

Here, the term "composite" refers to a state shown in FIG. 1 where a noble metal 2 and a transition metal compound 3 contact with each other on the same porous carrier 4 in an exhaust-gas purifying catalyst 1. As described above, in a state where the noble metal 2 and transition metal compound 3 contact with each other, the transition metal compound 3 is activated by virtue of spillover and acts as a catalytic site, thereby improving the catalytic activity. This allows to obtain an effect that the catalytic activity of the noble metal is

supplemented by the transition metal compound, thereby decreasing a usage amount of the noble metal. Further, the same effect as FIG. 1 can be obtained even in a state of another exhaust-gas purifying catalyst 11 shown in FIG. 2 which includes a noble metal 12 carried on a transition metal compound 13 which is in turn carried on a porous carrier 14.

Note that examples of the porous carrier include a porous substances such as alumina (aluminum oxide) and the like. Alumina including co-catalyst components such as Ti (titanium), Zr (zirconium) or the like, is capable of restricting degradation of the noble metal and transition metal compound and capable of improving the heat resistance of the alumina, thereby enabling to obtain an excellent exhaust-gas purifying catalyst. Additionally, the transition metal compound is in a state of simple oxide, complex oxide or alloy, and preferably has a metallic portion. By virtue of spillover, a portion of the transition metal compound contacts with a reducing gas within exhaust gas, so that a portion of the transition metal included in the transition metal compound is brought to have a valence of zero, i.e., the transition metal compound is brought to have a metallic portion. In this case, the catalytic activity is higher and the exhaust-gas purifying efficiency is improved, as compared with a state where the transition metal compound is oxide. Note that an interface between the porous carrier and the transition metal compound may form a complex oxide.

The transition metal element included in the transition metal compound and the noble metal, both contained in the exhaust-gas purifying catalyst, are preferably 0.01 to 35 in weight ratio Bw/Aw therebetween. Weight ratios Bw/Aw less than 0.01 lead to the decreased number of contacted interfaces between the noble metal and transition metal compound, thereby making it difficult to obtain due catalytic activities, because the activation of the transition metal compound by virtue of spillover of the reducing gases (such as HC, H_2, and CO) is

insufficient then. Further, the purpose to decrease the amount of the noble metal can not be achieved. In turn, Bw/Aw larger than 35 increase carried amounts of the transition metal compound, thereby decreasing the number of contacted interfaces, failing to obtain due catalytic activities. Further, in some cases, the transition metal compound clogs pores of the porous substance such as aluminum oxide acting as the carrier, thereby bringing about a situation where a sufficient catalytic activity is scarcely obtained.

It is further preferable that the noble metal is 0.7g or less in amount per 1L of exhaust-gas purifying catalyst. Although there has been a tendency that the catalytic activity is considerably lowered as the amount of the noble metal is decreased when the noble metal is 0.7g or less per 1L of exhaust-gas purifying catalyst in a case of solely using the noble metal as the conventional, there can be kept an excellent catalytic ability even in a region of 0.7g or less per 1L of exhaust-gas purifying catalyst in a state where the noble metal and transition metal compound contact with each other because the transition metal compound then acts as a catalytic site by virtue of spillover.

Note that amounts of noble metal greater than 0.7g per 1L of exhaust-gas purifying catalyst easily cause the noble metal to mainly act as a catalytic active site, thereby falling in a situation that the improvement of exhaust-gas purifying performance is hardly obtained in view of the increased cost.

It is more preferable that the amount of the noble metal is 0.5g or less per 1L of exhaust-gas purifying catalyst. In this case, the effect of the decreased amount of the noble metal becomes more remarkable.

It is further desirable that the porous carrier contains at least one kind of rare earth element selected from Sc (scandium), Y (yttrium), La (lanthanum), Ce (cerium), Pr (praseodymium), and Nd (neodymium). When the porous carrier carrying the noble metal and transition metal

compound contains the rare earth element, the above-mentioned catalyst activating effect by virtue of spillover is readily obtained.

The improved catalytic activity is considered to be based on a fact that the rare earth element can exhibit a plurality of oxidation states. For example, in case that the atmosphere of exhaust gas is in a lean state, i.e., when oxygen is excessive, there is a possibility that oxidation of the transition metal compound provided as a new catalytic site as well as catalytic activity degradation are easily caused. Nonetheless, in the lean state, the rare earth element contained in the porous substance is capable of occluding oxygen, because the rare earth element has a higher affinity with oxygen. It is thus considered that the above-mentioned oxidation of the transition metal compound can be restricted so that the deterioration of the catalytic activity can be prevented. In case that the atmosphere of exhaust gas is in a rich state, i.e., when oxygen is insufficient, the rare earth element releases oxygen to thereby obtain a reducing state so that the exhaust-gas purifying reaction is progressed. In this way, the exhaust-gas purifying catalyst according to the embodiment of the present invention can be used in any of lean, stoichiometric and rich exhaust-gas atmospheres.

Further, it is more desirable that the transition metal element included in the transition metal compound and the noble metal are 0.5 to 100 in particle diameter ratio Br/Ar therebetween. This particle diameter ratio Br/Ar is largely affected by carried concentrations of the noble metal and transition metal compound on the porous carrier. The expression that the particle diameter ratio Br/Ar is less than 0.5 means that the particle diameter Br of the transition metal compound is small or the particle diameter Ar of the noble metal is large. In this case, contact between the transition metal compound and noble metal is small, thereby meaning a state where the transition metal compound is solely carried on the porous carrier or the dispersibility of the noble metal is lowered. Thus, the region

where Br/Ar is smaller than 0.5 leads to a state where spillover rarely occurs, thereby making it difficult to obtain a sufficient catalytic activity. Meanwhile, in case that Br/Ar is larger than 100, the particle diameter Br of the transition metal compound becomes extremely large, thereby also resulting in a state where the effect by virtue of spillover is rarely obtained.

It is desirable that the rare earth element contained in the porous carrier and the transition metal element included in the transition metal compound are 0.1 to 5 in weight ratio Cw/Bw therebetween. When Cw/Bw is greater than 5, this is a state where the rare earth element is so much or the transition metal compound is less. Thus, this is a state where the catalytic activity is rarely obtained even when the catalytic activity deterioration of the transition metal compound is avoided by the rare earth element, because the amount of the transition metal compound is less in itself. Meanwhile, when Cw/Bw is less than 0.1, the rare earth element becomes less relative to the transition metal compound, thereby making it difficult to obtain the effect by virtue of removal of oxygen from the transition metal compound.

It is preferable that the ratio of the transition metal in a metallic state relative to the transition metal compound is 5% or more. In this case, the transition metal compound exhibits an effect as a three way catalyst which is a role of a catalyst for vehicle, thereby purifying HC, CO and NOx in exhaust gas at a good efficiency.

Although the exhaust-gas purifying catalyst according to the present invention will be concretely described based on Example 1 through Example 15 and Comparative Example 1 through Comparative Example 11, the scope of the present invention is not limited to these Examples. These Examples are to study the effectiveness of the exhaust-gas purifying catalyst according to the present invention, in a manner to show Examples of exhaust-gas purifying catalysts prepared

from different materials.

<Preparation of Specimens>

(Example 1)

Impregnated by immersion into a γ-alumina as a porous carrier was an aqueous mixture solution of a dinitro-diamine Pt nitric acid-acidic aqueous solution and a Co(II) nitrate hexahydrate such that Pt was 0.3% and Co was 5.0% when calculated as elements, respectively, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow, thereby obtaining a catalyst powder. Thereafter, 500g of the obtained catalyst powder, 50g of boehmite, and 1,570g of 10% nitric-acid-containing aqueous solution were charged into an alumina-made porcelain pot, and shaken and ground together with alumina balls, thereby obtaining a catalyst slurry. Further, this catalyst slurry was loaded onto a honeycomb substrate made of cordierite (900 cell/2.5 mil) and an excessive slurry was removed by airflow, followed by drying at 120°C and firing thereafter at 400°C in airflow, thereby coating the catalyst powder onto the honeycomb substrate to obtain an intended exhaust-gas purifying catalyst. Herein, the numerical value accompanied by the unit "cell" represents the number of cells per 1 inch (about 2.54cm) square of honeycomb. In turn, the numerical value accompanied by the term "mil" represents a wall thickness of honeycomb, and 1 mil is a length of thousandth inch (about 25.4μm).

(Example 2)

The same procedure as the Example 1 was conducted while adopting an Ni(II) nitrate hexahydrate instead of Co(II) nitrate hexahydrate, thereby obtaining a specimen of Example 2.

(Example 3)

Upon preparation of the catalyst powder in Example 1, Fe(III) nitrate nonahydrate was added instead of Co(II) nitrate hexahydrate such that Fe was 5.0% when calculated as an element, and it was

impregnated by immersion into a γ-alumina as a porous carrier carrying 3% of Ti, then dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Example 3.

(Example 4)

Upon preparation of the catalyst powder in Example 2, the same procedure as the Example 2 was conducted, except that addition of dinitro-diamine Pt nitric acid-acidic aqueous solution and a Co(II) nitrate hexahydrate was conducted such that Pt was 0.7% and Co was 10.0% when calculated as elements, respectively, thereby obtaining a specimen of Example 4.

(Example 5)

Upon preparation of the catalyst powder in Example 2, the same procedure as the Example 2 was conducted, except that Pd nitrate aqueous solution was used instead of dinitro-diamine Pt nitric acid-acidic aqueous solution and an Ni(II) nitrate hexahydrate was used instead of Co(II) nitrate hexahydrate, and the addition of them was conducted such that Pd was 0.3% and Ni was 0.5% when calculated as elements, respectively, thereby obtaining a specimen of Example 5.

(Example 6)

Impregnated by immersion into a γ-alumina as a porous carrier carrying 3% of Zr was an aqueous mixture solution of an Rh nitrate aqueous solution and an Fe(III) nitrate nonahydrate such that Rh was 0.3% and Fe was 5.0% when calculated as elements, respectively, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Example 6.

(Example 7)

Impregnated into a γ-alumina as a porous carrier was an aqueous mixture solution of a dinitro-diamine Pt nitric acid-acidic aqueous

solution and an Mn(II) nitrate hexahydrate instead of Co(II) nitrate hexahydrate such that Pt was 0.1% and Mn was 3.5% when calculated as elements, respectively, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Example 7.

(Example 8)

Impregnated into a γ-alumina as a porous carrier was an aqueous mixture solution of a dinitro-diamine Pt nitric acid-acidic aqueous solution and a Zn nitrate hexahydrate instead of Co(II) nitrate hexahydrate such that Pt was 0.35% and Zn was 0.3% when calculated as elements, respectively, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Example 8.

(Example 9)

Impregnated by immersion into a γ-alumina as a porous carrier was an aqueous mixture solution of a dinitro-diamine Pt nitric acid-acidic aqueous solution and a Co(II) nitrate hexahydrate such that Pt was 0.5% and Co was 10.0% when calculated as elements, respectively, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Example 9.

(Example 10)

Impregnated into a γ-alumina as a porous carrier was an aqueous solution containing Ce(III) nitrate hexahydrate, and it was dried at 150°C and then fired at 400°C×1 hour in airflow, thereby obtaining a γ-alumina carrying 9 wt% of Ce when calculated as oxide (CeO_2). Thereafter, the obtained Ce-carrying γ-alumina was impregnated, by immersion, with an aqueous mixture solution of a dinitro-diamine Pt nitric acid-acidic aqueous solution and a Co(II) nitrate hexahydrate such that Pt was 0.3% and Co was 5.0% when calculated as elements, respectively, and then it

was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Example 10.

(Example 11)

Impregnated into a γ-alumina as a porous carrier was an aqueous solution containing an Nd nitrate hexahydrate, and it was dried at 150°C and then fired at 400°C×1 hour in airflow, thereby obtaining a γ-alumina carrying 3 wt% of Nd when calculated as oxide (Nd_2O_3). Thereafter, the obtained Nd-carrying γ-alumina was impregnated, by immersion, with an aqueous mixture solution of a dinitro-diamine Pt nitric acid-acidic aqueous solution and an Fe (III) nitrate nonahydrate such that Pt was 0.3% and Fe was 5.0% when calculated as elements, respectively, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Example 11.

(Example 12)

Impregnated by immersion into a γ-alumina as a porous carrier was an aqueous mixture solution of an Au chloride aqueous acidic solution and an Ni(II) nitrate hexahydrate such that Au was 0.5% and Ni was 10.0% when calculated as elements, respectively, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Example 12.

(Example 13)

Impregnated into a γ-alumina as a porous carrier carrying 3% of Zr was an aqueous solution containing a Y nitrate hydrate, and it was dried at 150°C and then fired at 400°C×1 hour in airflow, thereby obtaining a γ-alumina carrying 6.7 wt% of Y-Zr when calculated as oxide (Y_2O_3). Thereafter, the obtained Y-Zr-carrying γ-alumina was impregnated, by immersion, with an aqueous mixture solution of a

dinitro-diamine Pt nitric acid-acidic aqueous solution and an Ni(II) nitrate hexahydrate such that Pt was 0.3% and Ni was 5.0% when calculated as elements, respectively, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Example 13.

(Example 14)

Impregnated into a γ-alumina as a porous carrier was an aqueous solution containing an La nitrate hydrate, and it was dried at 150°C and then fired at 400°C×1 hour in airflow, thereby obtaining a γ-alumina carrying 16 wt% of La when calculated as oxide (La_2O_3). Thereafter, the obtained La-Zr-carrying γ-alumina was impregnated, by immersion, with an aqueous mixture solution of a dinitro-diamine Pt nitric acid-acidic aqueous solution and a Co(II) nitrate hexahydrate such that Pt was 0.1% and Co was 3.3% when calculated as elements, respectively, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Example 14.

(Example 15)

Impregnated into a γ-alumina as a porous carrier carrying 3% of Zr was an aqueous solution containing a Pr nitrate (n)hydrate (n=4 to 6), and it was dried at 150°C and then fired at 400°C×1 hour in airflow, thereby obtaining a γ-alumina carrying 16 wt% of Pr-Zr when calculated as oxide. Thereafter, the obtained La-Zr-carrying γ-alumina was impregnated, by immersion, with an aqueous mixture solution of an Rh nitrate aqueous solution and a Co(II) nitrate hexahydrate such that Rh was 0.3% and Co was 8.0% when calculated as elements, respectively, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Example 15.

(Comparative Example 1)

Impregnated by immersion into a γ-alumina as a porous carrier was a dinitro-diamine Pt nitric acid-acidic aqueous solution such that Pt was 0.3% when calculated as an element, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. 500g of the obtained catalyst powder, 50g of boehmite, and 1,570g of 10% nitric-acid-containing aqueous solution were charged into an alumina-made porcelain pot, and shaken and ground together with alumina balls, thereby obtaining a catalyst slurry. Further, this catalyst slurry was loaded onto a honeycomb substrate made of cordierite (900 cell/2.5 mil) and an excessive slurry was removed in airflow, followed by drying at 120°C and firing thereafter at 400°C in airflow, thereby coating the catalyst powder onto the honeycomb substrate to obtain a specimen of Comparative Example 1.

(Comparative Example 2)

Impregnated by immersion into a γ-alumina as a porous carrier was an aqueous mixture solution of a dinitro-diamine Pt nitric acid-acidic aqueous solution and a Co(II) nitrate hexahydrate such that Pt was 3.0% and Co was 5.0% when calculated as elements, respectively, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Comparative Example 2.

(Comparative Example 3)

Impregnated by immersion into a γ-alumina as a porous carrier was a dinitro-diamine Pt nitric acid-acidic aqueous solution such that Pt was 3.0% when calculated as an element, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Comparative Example 3.

(Comparative Example 4)

Impregnated by immersion into a γ-alumina as a porous carrier was a dinitro-diamine Pt nitric acid-acidic aqueous solution such that Pt was 0.7% when calculated as an element, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Comparative Example 4.

(Comparative Example 5)

Impregnated by immersion into a γ-alumina as a porous carrier was a Pd nitrate aqueous solution such that Pd was 0.3% when calculated as an element, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Comparative Example 5.

(Comparative Example 6)

Impregnated by immersion into a γ-alumina as a porous carrier carrying 3% of Zr was an Rh nitrate aqueous solution such that Rh was 0.3% when calculated as an element, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Comparative Example 6.

(Comparative Example 7)

Impregnated by immersion into a γ-alumina as a porous carrier was an aqueous solution containing a Co(II) nitrate hexahydrate such that Co was 5.0% when calculated as an element, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Comparative Example 7.

(Comparative Example 8)

Impregnated by immersion into a γ-alumina as a porous carrier was a dinitro-diamine Pt nitric acid-acidic aqueous solution such that Pt

was 0.5% when calculated as an element, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Comparative Example 8.

(Comparative Example 9)

Charged into an alumina-made porcelain pot were 250g of the catalyst powder obtained in Comparative Example 1, 250g of the catalyst powder obtained in Comparative Example 7, 50g of boehmite, and 1,570g of 10% nitric-acid-containing aqueous solution, and they were shaken and ground together with alumina balls, thereby obtaining a catalyst slurry. Further, this catalyst slurry was loaded onto a honeycomb substrate made of cordierite (900 cell/2.5 mil) and an excessive slurry was removed in airflow, followed by drying at 120°C and firing thereafter at 400°C, thereby coating the catalyst powder onto the honeycomb substrate to obtain a specimen of Comparative Example 9.

(Comparative Example 10)

Impregnated by immersion into a γ-alumina as a porous carrier was an Au chloride acid such that Au was 0.5% when calculated as an element, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Comparative Example 10.

(Comparative Example 11)

Impregnated by immersion into a γ-alumina as a porous carrier was a dinitro-diamine Pt nitric acid-acidic aqueous solution such that Pt was 0.1% when calculated as an element, and then it was dried at 150°C×20 hours, followed by firing at 400°C×1 hour in airflow. Thereafter, the same procedure as Example 1 was conducted, to obtain a specimen of Comparative Example 11.

Here, the specimens obtained in the above specimen preparation were evaluated in the following manner.

<Catalyst Durability Test>

The durability test was conducted by setting a temperature of a catalyst inlet at 700°C in a V-type 6-cylinder engine manufactured by Nissan Motor Co., Ltd. Note that lead-free gasoline was used as a fuel.

<Catalyst Evaluation Test>

Catalyst evaluation was conducted based on a catalyst volume of 40cm^3 by cutting out a part of the catalyst carrier with the durability applied thereto. This was conducted under the conditions of a flow rate of reaction gas of 40L/minute, a reaction gas temperature of 350°C, and a reaction gas composition listed in the following Table 1.

[Table 1]

Reaction Gas Composition

Gas composition	Stoichiometric
Z value(-)	1.000
A/F(-)	14.5
NO (ppm)	1,000
CO(%)	0.6
H_2(%)	0.2
O_2(%)	0.6
CO_2(%)	13.9
HC(ppmC)	1665
H_2O(%)	10
N_2	balance

<Measurement of particle diameters of noble metal and transition metal compound>

Evaluation was performed based on TEM-EDX measurement, by scraping down a catalyst layer from each exhaust-gas purifying catalyst obtained by the above specimen preparation. The measurement was conducted by using an HF-2000 manufactured by Hitachi, Ltd., at an accelerating voltage of 200kV and a cutting condition of ordinary temperature. The measuring method was to embed the catalyst powder in

an epoxy resin, and to prepare an ultra-thin slice by an ultra-microtome after the epoxy resin had cured. Dispersed states of various crystal grains were investigated by a transmission electron microscope (TEM), by using the slice. Contrasted (shadow) parts in the obtained image were focused to determine metal kinds, to measure particle diameters (Ar and Br) of the metals, respectively.

<Measurement of reduced state of transition metal compound>

Qualitative, quantitative and state analyses of the elements of each specimen were conducted by X-ray photoelectron spectroscopy (XPS). Measurement was conducted by fixing the specimen on an indium foil while adopting a complex-type surface analyzing apparatus manufactured by PHI, under the condition that the X-ray source was Al-Kα ray (1486.6eV, 300W), the photoelectron extraction angle was 45° (measurement depth of 4nm), and the measuring area was 2mm×0.8mm. Upon measurement, hydrogen (hydrogen 0.2%/nitrogen) as one of compositions of exhaust gas was exposed at 400°C×10 minutes within a pretreatment chamber attached to the XPS apparatus, and then the XPS measurement was performed. Concerning a result of XPS measurement represented by reference numeral 21 in FIG. 3, peak separation was conducted by curve fitting. As shown in FIG. 3, bound energy values and half-widths of components 22 through 24 included in each transition metal compound were inputted into a Gaussian function (100%), and calculation was conducted by setting that a sum of surface areas of the components 22 through 24 became equal to a surface area of the measurement result 21 obtained by XPS measurement. The obtained surface area of the transition metal compound 24 in a metallic state was represented by B(0), the surface area of the whole of the transition metal compound 21 was represented by B(X), and there was calculated B(0)/B(X) in terms of percent to obtain a ratio of the transition metal in a metallic state to the transition metal compound carried by a carrier. Note

that, when the transition metal is Co, reference numeral 22 represents a high-oxidized transition metal such as cobalt aluminate ($CoAl_2O_4$), and reference numeral 23 represents an oxidized transition metal compound such as cobalt oxide (CoO).

Shown in the following Table 2 through Table 7 are evaluation results of the specimens in the Example 1 through Example 15 and Comparative Example 1 through Comparative Example 11.

[Table 2]

	Noble metal		Transition metal compound		Rare earthmetal		Carrier
	Kind	Carried conc. (%)	Tran. met element	Carried conc.(%)	Kind	Carried conc.(%)	
Ex.1	Pt	0.30	Co	5.0	-	-	γ-alumina
Ex.2	Pt	0.30	Ni	5.0	-	-	γ-alumina
Ex.3	Pt	0.30	Fe	5.0	-	-	Ti 3%/ γ-alumina
Ex.4	Pt	0.70	Co	10.0	-	-	γ-alumina
Ex.5	Pd	0.30	Ni	0.5	-	-	γ-alumina
Ex.6	Rh	0.30	Fe	5.0	-	-	Zr 3%/ γ-alumina
Ex.7	Pt	0.10	Mn	3.5	-	-	γ-alumina
Ex.8	Pt	0.35	Zn	0.3	-	-	γ-alumina
Ex.9	Pt	0.50	Co	10.0	-	-	γ-alumina
Ex.10	Pt	0.30	Co	5.0	Ce	9	γ-alumina
Ex.11	Pt	0.30	Fe	5.0	Nd	3	γ-alumina
Ex.12	Au	0.50	Ni	10.0	-	-	γ-alumina
Ex.13	Pt	0.30	Ni	5.0	Y	6.7	Zr 3%/ γ-alumina
Ex.14	Pt	0.10	Co	3.3	La	16	γ-alumina
Ex.15	Rh	0.30	Co	8.0	Pr	16	Zr 3%/ γ-alumina

[Table 3]

	Noble metal		Transition metal compound		Rare earthmetal		Carrier
	Kind	Carried conc. (%)	Tran. met element	Carried conc.(%)	Kind	Carried conc.(%)	
Com.Ex.1	Pt	0.30	-	-	-	-	γ-alumina
Com.Ex.2	Pt	3.00	Co	5.0	-	-	γ-alumina
Com.Ex.3	Pt	3.00	-	-	-	-	γ-alumina
Com.Ex.4	Pt	0.70	-	-	-	-	γ-alumina
Com.Ex.5	Pd	0.30	-	-	-	-	γ-alumina
Com.Ex.6	Rh	0.30	-	-	-	-	Zr 3%/ γ-alumina
Com.Ex.7	-	-	Co	5.0	-	-	γ-alumina
Com.Ex.8	Pt	0.50	-	-	-	-	γ-alumina
Com.Ex.9	Pt	0.30	Co	5.0	-	-	γ-alumina
Com.Ex.10	Au	0.50	-	-	-	-	γ-alumina
Com.Ex.11	Pt	0.10	-	-	-	-	γ-alumina

[Table 4]

	Coated Amount of cat. Powder onto honeycomb substrate (g/L)	Aw (g/L)	Bw (g/L)	Bw/Aw	Ar (nm)	Br (nm)	Br/Ar
Ex.1	110	0.30	5.0	16.7	4.8	55	11.5
Ex.2	110	0.30	5.0	16.7	5.3	43	8.1
Ex.3	110	0.30	5.0	16.7	5.2	63	12.1
Ex.4	110	0.70	10.0	14.3	4.9	83	16.9
Ex.5	110	0.30	0.5	1.7	5.0	62	12.4
Ex.6	110	0.30	5.0	16.7	2.8	96	34.3
Ex.7	330	0.10	3.5	35.0	1.0	76	76.0
Ex.8	110	0.35	0.3	0.9	5.3	35	6.6
Ex.9	110	0.50	10.0	20.0	7.3	73	10.0
Ex.10	110	0.30	5.0	16.7	3.9	55	14.1
Ex.11	110	0.30	5.0	16.7	5.0	65	13.0
Ex.12	110	0.50	10.0	20.0	7.6	68	8.9
Ex.13	110	0.30	5.0	16.7	5.0	43	8.6
Ex.14	110	0.10	3.3	33.0	1.3	32	24.6
Ex.15	110	0.30	8.0	26.7	0.9	86	95.6

[Table 5]

	Coated Amount of cat. Powder onto honeycomb substrate (g/L)	Aw (g/L)	Bw (g/L)	Bw/Aw	Ar (nm)	Br (nm)	Br/Ar
Com.Ex.1	110	0.30	-	-	4.6	-	-
Com.Ex.2	110	3.00	5.0	1.7	21.0	56	2.7
Com.Ex.3	110	3.00	-	-	26.0	-	-
Com.Ex.4	110	0.70	-	-	10.5	-	-
Com.Ex.5	110	0.30	-	-	4.9	-	-
Com.Ex.6	110	0.30	-	-	2.3	-	-
Com.Ex.7	110	-	5.0	-	-	48	-
Com.Ex.8	110	0.50	-	-	13.0	-	-
Com.Ex.9	220	0.30	5.0	16.7	-	-	-
Com.Ex.10	110	0.50	-	-	7.9	-	-
Com.Ex.11	110	0.10	-	-	1.0	-	-

[Table 6]

	Cw (g/L)	Cw/Bw	B(0)/B(X)	Purifying ratio (%)
Ex.1	-	-	5.2	54
Ex.2	-	-	7.3	51
Ex.3	-	-	5.0	48
Ex.4	-	-	8.3	58
Ex.5	-	-	5.1	45
Ex.6	-	-	6.3	73
Ex.7	-	-	5.5	57
Ex.8	-	-	7.3	38
Ex.9	-	-	6.9	63
Ex.10	9	1.8	5.7	63
Ex.11	3	0.6	5.9	59
Ex.12	-	-	5.6	26
Ex.13	6.7	1.3	6.9	55
Ex.14	16	4.8	10.2	57
Ex.15	16	2.0	8.6	65

[Table 7]

	Cw (g/L)	Cw/Bw	B(0)/B(X)	Purifying ratio (%)
Com.Ex.1	-	-	-	9
Com.Ex.2	-	-	7.6	55
Com.Ex.3	-	-	-	53
Com.Ex.4	-	-	-	38
Com.Ex.5	-	-	-	26
Com.Ex.6	-	-	-	51
Com.Ex.7	-	-	0.6	0.2
Com.Ex.8	-	-	-	11
Com.Ex.9	-	-	0.6	10
Com.Ex.10	-	-	-	5
Com.Ex.11	-	-	-	3

Shown in Table 2 are carried concentrations of elements included in specimens, weights (Aw, Bw and Cw) of the elements per 1L of specimen, weight ratios (Bw/Aw and Cw/Bw) of the included elements per 1L of specimen, particle diameter ratio Br/Ar, occupying ratio B(0)/B(X) of each transition metal compound B(0) in a metallic state to the whole of the transition metal compound, and purifying ratio after the durability test.

In Example 1, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Pt) was 0.3%, the carried concentration of transition metal element Co was 5.0%, the weight Aw of noble metal (Pt) per 1L of honeycomb substrate was 0.3g, the weight Bw of transition metal element Co included in transition metal compound was 5.0g, and Bw/Aw was 16.7. Further, the particle diameter Ar of noble metal (Pt) was 4.8nm, the particle diameter Br of transition metal element Co included in transition metal compound was 55nm, and Br/Ar was 11.5. The ratio B(0)/B(X) of the transition metal compound B(0) in a metallic state to the whole of the transition metal compound was 5.2. The purifying ratio after durability test was 54%.

In Example 2, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Pt) was 0.3%, the carried concentration of transition metal element Ni was 5.0%, the weight Aw of noble metal (Pt) per 1L of honeycomb substrate was 0.3g, the weight Bw of transition metal element Ni included in transition metal compound was 5.0g, and Bw/Aw was 16.7. Further, the particle diameter Ar of noble metal (Pt) was 5.3nm, the particle diameter Br of transition metal element Ni included in transition metal compound was 43nm, Br/Ar was

8.1, B(0)/B(X) was 7.3, and the purifying ratio after durability test was 51%.

In Example 3, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Pt) was 0.3%, the carried concentration of transition metal element Fe was 5.0%, the weight Aw of noble metal (Pt) per 1L of honeycomb substrate was 0.3g, the weight Bw of transition metal element Fe included in transition metal compound was 5.0g, and Bw/Aw was 16.7. Further, the particle diameter Ar of noble metal (Pt) was 5.2nm, the particle diameter Br of transition metal element Fe included in transition metal compound was 63nm, Br/Ar was 12.1, B(0)/B(X) was 5.0, and the purifying ratio after durability test was 48%.

In Example 4, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Pt) was 0.7%, the carried concentration of transition metal element Co was 10.0%, the weight Aw of noble metal (Pt) per 1L of honeycomb substrate was 0.7g, the weight Bw of transition metal element Co included in transition metal compound was 10.0g, and Bw/Aw was 14.3. Further, the particle diameter Ar of noble metal (Pt) was 4.9nm, the particle diameter Br of transition metal element Co included in transition metal compound was 83nm, Br/Ar was 16.9, B(0)/B(X) was 8.3, and the purifying ratio after durability test was 58%. It was found that a higher purifying ratio could be obtained identically to Example 1.

In Example 5, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Pd) was 0.3%, the carried concentration of transition metal element Ni was 0.5%, the weight Aw of noble metal (Pd) per 1L of honeycomb substrate was 0.3g, the weight Bw

of transition metal element Ni included in transition metal compound was 0.5g, and Bw/Aw was 1.7. Further, the particle diameter Ar of noble metal (Pt) was 5.0nm, the particle diameter Br of transition metal element Ni included in transition metal compound was 62nm, Br/Ar was 12.4, B(0)/B(X) was 5.1, and the purifying ratio after durability test was 45%.

In Example 6, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Rh) was 0.3%, the carried concentration of transition metal element Fe was 5.0%, the weight Aw of noble metal (Rh) per 1L of honeycomb substrate was 0.3g, the weight Bw of transition metal element Fe included in transition metal compound was 5.0g, and Bw/Aw was 16.7. Further, the particle diameter Ar of noble metal (Pt) was 2.8nm, the particle diameter Br of transition metal element Fe included in transition metal compound was 96nm, Br/Ar was 34.3, B(0)/B(X) was 6.3, and the purifying ratio after durability test was 73%.

In Example 7, the catalyst amount coated on the obtained honeycomb substrate was 330g per 1L of honeycomb substrate, the carried concentration of noble metal (Pt) was 0.1%, the carried concentration of transition metal element Mn was 3.5%, the weight Aw of noble metal (Pt) per 1L of honeycomb substrate was 0.3g, the weight Bw of transition metal element Fe included in transition metal compound was 10.5g, and Bw/Aw was 35.0. Further, the particle diameter Ar of noble metal (Pt) was 1.0nm, the particle diameter Br of transition metal element Fe included in transition metal compound was 76nm, Br/Ar was 76.0, B(0)/B(X) was 5.5, and the purifying ratio after durability test was 57%.

In Example 8, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the

carried concentration of noble metal (Pt) was 0.35%, the carried concentration of transition metal element Zn was 0.3%, the weight Aw of noble metal (Pt) per 1L of honeycomb substrate was 0.35g, the weight Bw of transition metal element Zn included in transition metal compound was 0.3g, and Bw/Aw was 0.9. Further, the particle diameter Ar of noble metal (Pt) was 5.3nm, the particle diameter Br of transition metal element Zn included in transition metal compound was 35nm, Br/Ar was 6.6, B(0)/B(X) was 7.3, and the purifying ratio after durability test was 38%.

In Example 9, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Pt) was 0.5%, the carried concentration of transition metal element Co was 10.0%, the weight Aw of noble metal (Pt) per 1L of honeycomb substrate was 0.5g, the weight Bw of transition metal element Co included in transition metal compound was 10.0g, and Bw/Aw was 20.0. Further, the particle diameter Ar of noble metal (Pt) was 7.3nm, the particle diameter Br of transition metal element Co included in transition metal compound was 73nm, Br/Ar was 10.0, B(0)/B(X) was 6.9, and the purifying ratio after durability test was 63%.

In Example 10, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Pt) was 0.3%, the carried concentration of transition metal element Co was 5.0%, the carried concentration of rare earth element Ce was 9% when calculated as oxide, the weight Aw of noble metal (Pt) per 1L of honeycomb substrate was 0.3g, the weight Bw of transition metal element Co included in transition metal compound was 5.0g, the weight Cw of rare earth element Ce was 9.0g, Bw/Aw was 16.7, and Cw/Bw was 1.8. Further, the particle diameter Ar of noble metal (Pt) was 3.9nm, the particle diameter Br of transition

metal element Co included in transition metal compound was 55nm, Br/Ar was 14.1, B(0)/B(X) was 5.7, and the purifying ratio after durability test was 63%.

In Example 11, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Pt) was 0.3%, the carried concentration of transition metal element Fe was 5.0%, the carried concentration of rare earth element Nd was 3% when calculated as oxide, the weight Aw of noble metal (Pt) per 1L of honeycomb substrate was 0.3g, the weight Bw of transition metal element Co included in transition metal compound was 5.0g, the weight Cw of rare earth element Nd was 3g, Bw/Aw was 16.7, and Cw/Bw was 0.6. Further, the particle diameter Ar of noble metal (Pt) was 5.0nm, the particle diameter Br of transition metal element Nd included in transition metal compound was 65nm, Br/Ar was 13.0, B(0)/B(X) was 5.9, and the purifying ratio after durability test was 59%.

In Example 12, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Au) was 0.5%, the carried concentration of transition metal element Ni was 10.0%, the weight Aw of noble metal (Au) per 1L of honeycomb substrate was 0.5g, the weight Bw of transition metal element Ni included in transition metal compound was 10.0g, and Bw/Aw was 20.0. Further, the particle diameter Ar of noble metal (Au) was 7.6nm, the particle diameter Br of transition metal element Ni included in transition metal compound was 68nm, Br/Ar was 8.9, B(0)/B(X) was 5.6, and the purifying ratio after durability test was 26%.

In Example 13, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Pt) was 0.3%, the carried

concentration of transition metal element Ni was 5.0%, the carried concentration of rare earth element Y was 6.7% when calculated as oxide, the weight Aw of noble metal (Pt) per 1L of honeycomb substrate was 0.3g, the weight Bw of transition metal element Ni included in transition metal compound was 5.0g, the weight Cw of rare earth element Y was 6.7g, Bw/Aw was 16.7, and Cw/Bw was 1.3. Further, the particle diameter Ar of noble metal (Pt) was 5.0nm, the particle diameter Br of transition metal element Ni included in transition metal compound was 43nm, and Br/Ar was 8.6. B(0)/B(X) was 6.9, and the purifying ratio after durability test was 55%.

In Example 14, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Pt) was 0.1%, the carried concentration of transition metal element Co was 3.3%, the carried concentration of rare earth element La was 16% when calculated as oxide, the weight Aw of noble metal (Pt) per 1L of honeycomb substrate was 0.1g, the weight Bw of transition metal element Co included in transition metal compound was 3.3g, the weight Cw of rare earth element La was 16.0g, Bw/Aw was 33.0, and Cw/Bw was 4.8. Further, the particle diameter Ar of noble metal (Pt) was 1.3nm, the particle diameter Br of transition metal element Co included in transition metal compound was 32nm, Br/Ar was 24.6, B(0)/B(X) was 10.2, and the purifying ratio after durability test was 57%.

In Example 15, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Rh) was 0.3%, the carried concentration of transition metal element Co was 8.0%, the carried concentration of rare earth element Pr was 16% when calculated as oxide, the weight Aw of noble metal (Rh) per 1L of honeycomb substrate was 0.3g, the weight Bw of transition metal element Co included in transition

metal compound was 8.0g, the weight Cw of rare earth element Pr was 16g, Bw/Aw was 26.7, and Cw/Bw was 2.0. Further, the particle diameter Ar of noble metal (Rh) was 0.9nm, the particle diameter Br of transition metal element Co included in transition metal compound was 86nm, and Br/Ar was 95.6. B(0)/B(X) was 8.6, and the purifying ratio after durability test was 65%.

In Comparative Example 1, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Pt) was 0.3%, and the weight Aw of noble metal (Pt) per 1L of honeycomb substrate was 0.3g. Further, the particle diameter Ar of noble metal (Pt) was 4.6nm, and the purifying ratio after durability test was 9%.

In Comparative Example 2, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Pt) was 3.0%, the carried concentration of transition metal element Co was 5.0%, the weight Aw of noble metal (Pt) per 1L of honeycomb substrate was 3.0g, the weight Bw of transition metal element Co included in transition metal compound was 5.0g, and Bw/Aw was 1.7. Further, the particle diameter Ar of noble metal (Pt) was 21.0nm, the particle diameter Br of transition metal element Co included in transition metal compound was 56.0nm, and Br/Ar was 2.7. B(0)/B(X) was 7.6, and the purifying ratio after durability test was 55%.

In Comparative Example 3, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Pt) was 3.0%, and the weight Aw of noble metal (Pt) per 1L of honeycomb substrate was 3.0g. Further, the particle diameter Ar of noble metal (Pt) was 26.0nm, and the purifying ratio after durability test was 53%.

In Comparative Example 4, the catalyst amount coated on the

obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Pt) was 0.7%, and the weight Aw of noble metal (Pt) per 1L of honeycomb substrate was 0.7g. Further, the particle diameter Ar of noble metal (Pt) was 10.5nm, and the purifying ratio after durability test was 38%.

In Comparative Example 5, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Pd) was 0.3%, and the weight Aw of noble metal (Pd) per 1L of honeycomb substrate was 0.3g. Further, the particle diameter Ar of noble metal (Pd) was 4.9nm, and the purifying ratio after durability test was 26%.

In Comparative Example 6, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Rh) was 0.3%, and the weight Aw of noble metal (Rh) per 1L of honeycomb substrate was 0.3g. Further, the particle diameter Ar of noble metal (Rh) was 2.3nm, and the purifying ratio after durability test was 51%.

In Comparative Example 7, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of transition metal element Co was 5.0%, the weight Bw of transition metal element Co included in transition metal compound was 5.0g. Further, the particle diameter Br of transition metal element Co included in transition metal compound was 48nm, B(0)/B(X) was 0.6, and the purifying ratio after durability test was 0.2%.

In Comparative Example 8, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Pt) was 0.5%, and the weight Aw of noble metal (Pt) per 1L of honeycomb substrate was 0.5g. Further, the particle diameter Ar of noble metal (Pt) was 13.0nm, and the purifying ratio after durability test was 11%.

In Comparative Example 9, the catalyst amount coated on the obtained honeycomb substrate was 220g per 1L of honeycomb substrate, the carried concentration of noble metal (Pt) was 0.3%, the carried concentration of transition metal element Co was 5.0%, the weight Aw of noble metal (Pt) per 1L of honeycomb substrate was 0.3g, the weight Bw of transition metal element Co included in transition metal compound was 5.0g, and Bw/Aw was 16.7. B(0)/B(X) was 0.6, and the purifying ratio after durability test was 10%.

In Comparative Example 10, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Au) was 0.5%, and the weight Aw of noble metal (Au) per 1L of honeycomb substrate was 0.5g. Further, the particle diameter Ar of noble metal (Au) was 7.9nm, and the purifying ratio after durability test was 5%.

In Comparative Example 11, the catalyst amount coated on the obtained honeycomb substrate was 110g per 1L of honeycomb substrate, the carried concentration of noble metal (Pt) was 0.1%, and the weight Aw of noble metal (Pt) per 1L of honeycomb substrate was 0.1g. Further, the particle diameter Ar of noble metal (Pt) was 1.0nm, and the purifying ratio after durability test was 3%.

FIG. 4 is a graph of purifying ratios after endurance in Examples 1, 10 and Comparative Examples 1, 2, 3 and 7. In FIG. 4, reference numeral 31 represents a purifying ratio of Example 1, and reference numerals 32, 33, 34, 35 and 36 represent the purifying ratios of Example 10 and Comparative Examples 1, 2, 3 and 7, respectively. Comparing 31 with 36 in FIG. 4, the purifying ratio was 0.2% in Comparative Example 7 represented by 36 when only the transition metal Co was carried so that catalytic activities were hardly obtained by the transition metal Co only. Contrary, it was found that the purifying ratio of Example 1 represented by 31 was largely improved to 270 times that of Comparative

Example 7, by carrying the noble metal (Pt) together with transition metal Co.

Further, comparing 31 with 33 in FIG. 4, it was found that, in Example 1 represented by 31 and Comparative Example 1 represented by 33, although the carried concentrations of the carried noble metal (Pt) were the same at 0.3% and the particle diameters Ar of the noble metal (Pt) took the analogous values, the purifying ratio of Example 1 was about 6 times as high as that of Comparative Example 1, thereby showing that the catalyst efficiency is largely improved by carriage of the transition metal element Co.

Comparing the values of Comparative Example 2 represented by 34 with those of Comparative Example 3 represented by 35, the carried concentrations of the carried noble metal (Pt) were the same at 3.0% and the values of purifying ratios were substantially the same, so that the catalytic effect by carriage of the transition metal element Co was inconsiderable. In turn, although the carried amount of the noble metal (Pt) in the specimen obtained in Comparative Example 2 was 10 times, the purifying ratios of Example 1 and Comparative Example 2 were substantially the same. Further, it was found from Comparative Example 7 represented by 36, that catalytic activities were hardly obtained by the transition metal element Co only. Based on these results, it was found that the simultaneous carriage of the transition metal element Co having few catalytic activities and the noble metal (Pt) makes it possible to obtain a catalytic activity which is the same as or superior to that in the situation where only the noble metal (Pt) is carried. It was further found that this effect is rather exhibited with lesser amounts of the noble metal (Pt), and that higher catalytic activities can be kept even when the noble metal (Pt) is decreased in amount.

Further, comparing Example 1 represented by 31 with Example 10 represented by 32, the purifying ratio of Example 10 was higher than

that of Example 1, thereby showing that the purifying ratio is further improved by the inclusion of rare earth element Ce in the porous carrier.

Also, the purifying ratios in Examples 2, 3 were improved as compared with Comparative Example 1, thereby showing that the purifying ratio is improved identically to Example 1 even by adopting transition metal elements Ni, Fe. In this way, it was found that higher purifying ratios are obtained in any one of transition metal elements Co, Ni, Fe when the carried concentration of noble metal (Pt) is 0.3% and the carried concentration of the transition metal element is 5.0%.

Also, the purifying ratio was improved in Example 4 as compared with Comparative Example 1, thereby showing that higher purifying ratios are obtained.

In Example 5, the purifying ratio was improved as compared with Comparative Example 1 though the amount of transition metal element Ni was as less as 1/10 as compared with Example 2, thereby showing that a certain degree of purifying ratio is obtained even when the amount of transition metal element Ni is small.

In Example 6, there was obtained an extremely high purifying ratio, thereby showing that the higher purifying ratio is obtained when the noble metal (Rh) and transition metal element Fe are carried by γ-alumina carrying 3% of Zr, at the carried concentration of 0.3% and the carried concentration 5.0%, respectively.

In Example 7, although the carried concentration of noble metal (Pt) was as low as 0.1%, there was obtained a higher purifying ratio identically to Example 1 by simultaneously carrying the transition metal element Mn.

In Example 8, the carried concentration of noble metal (Pt) was 0.35% and the carried concentration of transition metal element Zn was 0.3%, and the purifying ratio was improved as compared with Comparative Example 1.

In Example 9, there was obtained a higher purifying ratio, and it was presumed that the purifying ratio was higher than Example 1 because both the carried concentration of noble metal (Pt) and the carried concentration of transition metal element Co were higher as compared with Example 1.

In Example 11, it was found that the purifying ratio was further improved by inclusion of the rare earth element Nd into the porous carrier similarly to Example 10.

In Example 12, although there was not obtained a higher purifying ratio as compared with Example 1, it was found that the purifying ratio was improved by simultaneously carrying the transition metal element Ni, as compared with a case of the noble metal (Au) only in Comparative Example 10.

In Example 13, the purifying ratio was improved as compared with Example 2, thereby showing that the purifying ratio is improved in the case where the noble metal (Pt) and transition metal element Ni are carried by Y-Zr-carrying γ-alumina as compared with the case that the noble metal (Pt) and transition metal element Ni are carried by γ-alumina.

In Example 14, the purifying ratio was largely improved as compared with Comparative Example 11, thereby showing that the higher purifying ratio is obtained by virtue of the inclusion of rare earth element La in the porous carrier even when the carried concentration of noble metal (Pt) and the carried concentration of transition metal element Co are low.

In Example 15, the purifying ratio was improved as compared with Comparative Example 6, and there was obtained the higher purifying ratio. This showed that the higher purifying ratio was obtained when the noble metal (Rh) and transition metal element Co were carried by the Pr-Zr-carrying γ-alumina.

Note that the purifying ratio of the specimen obtained in Comparative Example 9 was about 1/5 as compared with Example 1, thereby showing that higher purifying ratios are not obtained unless the noble metal (Pt) and transition metal element Co are simultaneously carried by γ-alumina by immersion upon preparation of the catalyst powder.

FIG. 5 shows a relationship between carried concentration of Pt and purifying ratio, in exhaust-gas purifying catalysts prepared by adding transition metal thereto and exhaust-gas purifying catalysts without addition of transition metal. Reference numeral 41 in FIG. 5 represents purifying ratios when the carried concentration of Pt were 3%. Considering the purifying ratios 41 in FIG. 5, the values thereof were substantially unchanged between the case of preparation with addition of transition metal and the case of preparation without addition of transition metal, so that remarkable effects were not observed for addition of transition metal. Reference numeral 42 in FIG. 5 represents purifying ratios when the carried concentration of Pt were 0.7%. Comparing values of the purifying ratios 42 in FIG. 5, there was obtained a higher purifying ratio in case of preparation by addition of transition metal. Reference numeral 43 in FIG. 5 represents purifying ratios when the carried concentration of Pt were 0.3%. In view of the purifying ratios 43 in FIG. 5, there was observed a remarkable difference in purifying ratio between the case with addition of transition metal and the case without addition of transition metal. Reference numeral 44 in FIG. 5 represents purifying ratios when the carried concentration of Pt were 0.1%. In view of the purifying ratios 44 in FIG. 5, there was observed a more remarkable difference in purifying ratio between the case with addition of transition metal and the case without addition of transition metal, thereby showing that catalytic activities are maintained by addition of transition metal even in a decreased amount of Pt.

In this way, when the carried concentration of Pt was 0.7% or less, i.e., when the amount of Pt was 0.7g or less per 1L of exhaust-gas purifying catalyst volume, there was observed a remarkable effect to maintain the purifying ratios by virtue of addition of transition metal even when the usage amounts of Pt were decreased. It was further observed that sufficient catalytic activities were obtained by virtue of addition of transition metal even when amounts of Pt were decreased.

The present invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The embodiments are therefore to be considered in all aspects as illustrative and not restrictive, the scope of the present invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

INDUSTRIAL APPLICABILITY

The present invention has applicability in providing an exhaust-gas purifying catalyst capable of maintaining a higher catalytic activity even with a decreased amount of noble metal.